

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 087 309****A1**

(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **83300897.2**(51) Int. Cl.<sup>3</sup>: **C 23 C 13/04**(22) Date of filing: **21.02.83****C 23 C 13/02, B 05 D 1/36**

(30) Priority: **22.02.82 US 350437**  
**22.02.82 US 350722**  
**22.02.82 US 350724**

(43) Date of publication of application:  
**31.08.83 Bulletin 83/35**

(84) Designated Contracting States:  
**BE CH DE FR GB IT LI**

(71) Applicant: **MINNESOTA MINING AND  
MANUFACTURING COMPANY**  
**3M Center**  
**Saint Paul, Minnesota 55101(US)**

(72) Inventor: **Cederberg, Barbara M.**  
**c/o Minnesota Mining and Manufacturing Company**  
**P.O. Box 33427 St. Paul Minnesota 55133(US)**

(72) Inventor: **Downing, Edward J.**  
**c/o Minnesota Mining and Manufacturing Company**  
**P.O. Box 33427 St. Paul Minnesota 55133(US)**

(72) Inventor: **Fisch, Richard S.**  
**c/o Minnesota Mining and Manufacturing Company**  
**P.O. Box 33427 St. Paul Minnesota 55133(US)**

(74) Representative: **Bowman, Paul Alan et al.**  
**LLOYD WISE, TREGAR & CO. Norman House 105-109**  
**Strand**  
**London WC2R 0AE(GB)**

(54) **Protected vapor-deposited metal layers.**

(57) A process for improving the abrasion resistance of vapor deposited metal layers which comprises vapor depositing a metal layer on at least one surface of a substrate and, before subjecting the metal layer to physical treatment or contact which would abrade the metal layer, vapor depositing onto said metal layer 1) a 1 to 600 nm layer of organic material having a vapor pressure at 20°C equal to or less than that of 1-n-octanol said material having a) a carbonyl group not part of a carboxyl group, b) a phenoxy group, c) an ester group, or d) an alcohol group, or 2) a layer of organic material having a thickness of at least 1 nm and less than 30 nm and a) a carboxyl group b) a saccharide, c) Rhodamine B, or d) phthalocyanine. The organic materials can improve the properties of the metal layer when used in photoresist imaging films.

**EP 0 087 309 A1**

PROCESS FOR PROTECTING VAPOR-DEPOSITED METAL LAYERS

BACKGROUND OF THE INVENTION

Field of the Invention

5 This invention relates to vapor-deposited metal layers which are protected from damage by the application of an organic layer to its surface. The invention further relates to the process of applying the protective organic layer to the surface of the vapor-deposited metal layer and to the photosensitive articles made with the protected  
10 metal layer.

In particular, the present invention relates to the application of an organic layer onto the surface of a vapor deposited metal layer. The metal layer is generally formed on a supporting base by any of the various vapor-  
15 depositing techniques. Prior to subjecting the deposited metal layer to any physical treatments or stress likely to damage the continuity of the coating (e.g., rolling, folding, bending, and the like) an organic layer is vapor deposited onto the surface of the metal.

20 Description of the Prior Art

Vapor-deposited layers of metals, particularly those on flexible webs, tend to be soft and easily rubbed off. These defects are particularly unacceptable where such layers are to be used as part of an imaging system  
25 consisting of a vapor-deposited metal layer and an over-coated photoresist or photopolymer layer. Marks, scuffs, kinks, or abrasions in the metal layer produce voids or areas in the film which contain no useful image, thus interrupting the faithfulness of the image. These  
30 photographic defective areas have been called by various names such as pinholes, cinch marks, scuffs, etc., depending on where and how the abrasion was produced. In order to avoid such defects, a protective resin layer is generally coated on the metal layer. This is often done in  
35 a separate coating operation on a different coating

machine. The difficulty with this practice, however, is that the unprotected vapor-coated metal film must be wound after the vapor-coating operation to transport the material to the more conventional resin coater. Defects such as  
5 cinch marks, abrasions, and kinks are often produced during this winding operation.

In order to avoid the problems described above, several attempts have been made to vapor-deposit the metallic and organic layers in the same vacuum chamber,  
10 thus eliminating the need to wind the film in a roll between coating operations. One such process is described in U.S. 4,268,541. Here the vapor-deposition chamber is divided into 2 sections, by means of a partition, thereby separating the metal deposition area from the organic  
15 deposition section. Thus the organic protective layer is deposited over the metal layer without the need to rewind the roll in between the two coating operations.

The organic compounds used in U.S. Pat. 4,268,541 include polymers (for example, those derived from meth-  
20 acrylic acid and acrylic acid), low molecular weight organic compounds containing a carboxyl group (e.g., compounds such as abietic acid, isophthalic acid, behenic acid, terephthalic acid, phthalic acid, etc., and a few random compounds (e.g., Rhodamine B, rosin, a phthalocyanine, a monosaccharide, and an oligosaccharide).  
25

The technique and materials described in U.S. 4,268,541 have been found to be suitable for only limited uses. The layer thickness of 30-600 nm specified with those materials disclosed is not suitable for many imaging  
30 film constructions, and for many processing techniques. In particular, the friction properties of the coating cause layers of the coated material which are stacked or rolled to slide and move out of register. In rolled form, telescoping of the roll is quite serious. This can cause  
35 serious delays and expense in further use of the film.

Organic protection layers located between the metal layer and a photoresist layer can drastically affect

the oxidizing or etching step and the quality of the resulting image. For, example, excessive thickness of such layers may provide a preferential pathway for the developer or etch solution thereby resulting in image degradation or fine detail loss. This is especially true of material whose final designation is copy or contact reprographic work. Films such as these, called lith or contact films, depend on fine dot arrays to reproduce image tone. Fine dots (3-5%) may be undercut and etched away thereby degrading the quality of the reproduction.

The relatively thick layer of some acid-containing protective materials such as disclosed in U.S. Pat. No. 4,268,541 can also interfere with the etching of the metal by neutralizing the alkaline metal etching solution. Such neutralization inhibits the formation of an etched metal image and thus interferes with the formation of an image of acceptable quality.

Another attempt at overcoming the abrasion problems is described in Japanese patent publication number 56/9736. In this case, the metal and the organic compound are deliberately coated as a single layer; i.e., the metal and organic vapors are substantially mixed in the vapor stream before they are deposited on the support. This is not completely satisfactory because the heated metal vapor can carbonize or decompose the organic material resulting in an unacceptable product. Also, the thickness of the layer is required to be at least 20 to 1000 nm. The scope of organic materials is also quite specific and generally emphasizes organic acid materials.

#### SUMMARY OF THE INVENTION

The application of layers of organic material with a vapor pressure at 20°C no greater than 1-n-octanol said material having 1) carbonyl groups which are not part of carboxyl groups, 2) phenoxy groups, 3) ester groups, 4) urea groups, or 5) alcohol groups onto vapor-deposited metal surfaces has been found to provide excellent damage

resistance to the metal layer as coatings of 1 to 600 nm. Organic materials having 1) carboxyl groups, 2) polysaccharides, and 3) phthalocyanines provide excellent resistance in thickness of 1 to less than 30 nm. The  
5 presence of these organic materials on the vapor-deposited metal layer in photoresist imaging constructions provides for uniform development characteristics in the image. These materials reduce or eliminate the low friction  
10 properties attendant with the use of acids as protective layers, and because of reduced acidity these materials do not neutralize alkaline developing solutions as much as acid protective layers.

#### DETAILED DESCRIPTION OF THE INVENTION

The basic article of the present invention  
15 comprises a substrate, a vapor-deposited metal layer on at least one surface of said substrate, and a 1 to 600 nm protective organic layer on said metal layer comprising a material having phenoxy groups, alcohol groups, urea  
20 groups, ester groups, or carbonyl groups which are not part of carboxyl groups or a 1 to less than 30 nm organic layer of a 1) carboxyl containing compound 2) polysaccharide, 3) Rhodamine B or 4) phthalocyanine. In a preferred embodiment, a photoresist layer is coated over said  
protective layer.

25 The substrate may be any surface or material onto which metal may be vapor-deposited. The substrate may be rough or smooth, transparent or opaque, and continuous or porous. It may be of natural or synthetic polymeric resin (thermoplastic or thermoset), ceramic, glass, metal, paper,  
30 fabric, and the like. For most commercial purposes the substrate is preferably a polymeric resin such as polyester (e.g., polyethyleneterephthalate), cellulose ester, polycarbonate, polyvinyl resin (e.g., polyvinylchloride, polyvinylidene chloride, polyvinylbutyral, polyvinylformal),  
35 polyamide, polyimide, polyacrylate (e.g., copolymers and homopolymers of acrylic acid, methacrylic acid, n-butyl

0087309

acrylate, acrylic anhydride and the like), polyolefin, and the like. The polymer may be transparent, translucent or opaque. It may contain fillers such as carbon black, titania, zinc oxide, dyes, pigments, and of course, those materials generally used in the formation of films such as coating aids, lubricants, antioxidants, ultraviolet radiation absorbers, surfactants, catalysts and the like.

The vapor-deposited metal layer may be any vapor-deposited metal or metalloid layer. According to the practice of the present invention, the term metal layer is defined as a layer comprising metal, metal alloys, metal salts, and metal compounds. The corresponding meaning applies to the term metalloid layer. The term metal in metal layer is defined in the present invention to include semi-metals (i.e., metalloids) and semiconductor materials. Metals include materials such as aluminum, antimony, beryllium, bismuth, cadmium, chromium, cobalt, copper, gallium, germanium, gold, indium, iron, lead, magnesium, manganese, molybdenum, nickel, palladium, rhodium, selenium, silicon, silver, strontium, tellurium, tin, titanium, tungsten, vanadium, and zinc. Preferably the metal is selected from aluminum, chromium, nickel, tin, titanium and zinc. More preferably the metal is aluminum. Metal alloys such as aluminum-iron, aluminum-silver, bismuth-tin, and iron-cobalt alloys are included in the term metal layer and are particularly useful. Metal salts such as metal halides, metal carbonates, metal nitrates and the like are useful. Metal compounds such as metal oxides and metal sulfides are of particular utility in imaging systems. Metal layers comprising mixtures of these materials such as mixtures of metal-metal oxides, metal-metal salts, and metal salts-metal oxides are also of particular interest.

The thickness of the vapor-deposited metal layer depends upon the particular needs of the final product. In imaging constructions, for example, the thickness should be at least about 3 nm. Generally, the layer would be no

0087309

thicker than 750 nm which would require a long etching period. A more practical commercial range would be between 10 and 500 nm. A preferred range would be between 20 and 400 nm and a more preferred range would be between 25 and 300 nm or 30 and 200 nm.

It is preferred that the majority of the cross-section of the metal layer consist essentially of metal, metal alloys, metal salts and metal compounds. Traces of up to 10% or more of other materials may be tolerated generally in the layer, and in fact in certain processes of manufacture the boundary region of the metal layer and the protective layer may have a graded or gradual change from 100% metal to 100% organic material. But metal layers with the majority (at least 50%) of its cross-section consisting essentially of metals, metal alloys, metal salts, metal compounds and combinations thereof are preferred. The metal layer should have fewer than 100, preferably fewer than 50, and more preferably fewer than 30 defects per 177 mm<sup>2</sup>.

Vapor-deposition of the metal layer may be accomplished by any means. Thermal evaporation of the metal, ion plating, radio frequency sputtering, A.C. sputtering, D.C. sputtering and other known processes for deposition may be used in the practice of the present invention. The pressure may vary greatly during coating, but is usually in the range of 10<sup>-6</sup> to 10<sup>-4</sup> torr.

The organic protective layer which may be from 1 to 750 nm comprises a material with a vapor pressure at 20°C no greater than that of 1-n-octanol selected from the group consisting of 1) organic materials having carbonyl groups which are not part of carboxyl groups, 2) phenoxy groups, or 3) alcohols. The term "organic material" is used because the protective coating does not have to be a single compound or a monomeric compound. In addition to those types of materials, dimers, trimers, oligomers, polymers, copolymers, terpolymers and the like may be used.

The organic materials containing carbonyl groups which are not part of a carboxyl group, for example,

include 1) amides, such as phthalamide, salicylamide, urea formaldehyde resins, and methylene-bis-acrylamide, and 2) anilides, such as phthalanilide and salicylanilide. It has been found that these organic materials may be used in layers as thin as 1 nm and provide good abrasion or mar protection. They may be used in thicknesses of up to 600 nm, but without dramatic improvement of results, and in fact often with some diminution of properties. A preferred range would be between 3 and 200 nm, more preferably between 5 and 100 nm, and most preferably at least 5 and lower than 30 or 20 nm.

The organic material containing ester groups includes such materials as polyester oligomers, low molecular weight polyester polymers (e.g., polyethylene-terephthalate, polyethyleneisophthalate, etc. having molecular weights between 5,000 and 50,000), diallyl phthalate (and its polymers), diallyl isophthalate (and its polymers), monomethyl phthalate, carboxylic acid alkyl esters, and the like.

The organic material containing phenoxy groups include such materials as Bisphenol A, and low molecular weight phenol formaldehyde resins (e.g., Resinox®). The alcohol containing materials would include 1-n-octanol, dodecanol, benzyl alcohol and the like.

The organic protective layer comprises a material selected from the group consisting of organic materials having 1) carboxyl groups, 2) saccharide, or 3) phthalocyanine. Preferably these materials have a vapor pressure at 20°C which is not higher than that of 1-n-octanol. The term "organic material" is used because the protective coating does not have to be a single compound or a monomeric compound. In addition to those types of materials, dimers, trimers, oligomers, polymers, copolymers, terpolymers and the like may be used.

The organic materials containing a carboxyl group, for example, include aliphatic carboxylic acids, aromatic carboxylic acids, acrylates, polyacrylates,

copolyacrylates, polycarboxylic acids and the like as described in U.S. Patent 4,268,541.

5       The organic material should be vapor-depositable as this is the general method preferred for application of the protective layer. The organic material may, for example, be deposited in the apparatus and procedures disclosed in U.S. Patent No. 4,268,541. The partition or baffle described in that apparatus (e.g., Example 1) has not been found to be essential. The two vapor streams  
10       (i.e., metal and organic material streams) may be physically spaced apart or directed so that the coating zones for the two materials do not completely overlap. No serious problem has been found even when 50% of each of the coating zones overlap (so that at least 50% of the thick-  
15       ness of the metal layer consists essentially of metal, metal salts, metal compounds, and combinations thereof), although this is not a preferred construction. It is preferred that less than 25% of the total weight of the metal component be in such an overlapping or mixing zone  
20       and more preferably less than 10% or even 0% be in such zones. The recitation of a metal layer in the practice of the present invention requires, however, that at least a region of the coating, usually adjacent to the substrate, consists essentially of a metal layer without a dispersed  
25       phase of organic material therein.

      The photoresist layer may be either a negative-acting or positive acting photoresist as known in the art. Positive acting photoresist systems ordinarily comprise polymeric binders containing positive acting diazonium  
30       salts or resins such as those disclosed, for example, in U.S. Patents Nos. 3,046,120, 3,469,902 and 3,210,239. The positive acting photosensitizers are commercially available and are well reported in the literature. Negative acting photosensitive resist systems ordinarily comprise a poly-  
35       merizable composition which polymerizes in an imagewise fashion when irradiated, such as by exposure to light. These compositions are well reported in the literature and

are widely commercially available. These compositions ordinarily comprise ethylenically or polyethylenically unsaturated photopolymerizable materials, although photosensitive epoxy systems are also known in the art.

5 Preferably ethylenically unsaturated photopolymerizable systems are used, such as acrylate, methacrylate, acrylamide and allyl systems. Acrylic and methacrylic polymerizable systems are most preferred according to the practice of the present invention. U. S. Patents Nos.  
10 3,639,185, 4,247,616, 4,008,084, 4,138,262, 4,139,391, 4,158,079, 3,469,982, U.K. Patent No. 1,468,746, disclose photosensitive compositions generally useful in the practice of the present invention. U. S. Patent No. 4,314,022 discloses etchant solutions particularly useful  
15 in the practice of the present invention.

Light-sensitive imaging elements of the present invention can be provided with a print-out image system by bonding a layer which is at least partially impervious to the generated gas on the surface of the layer generating  
20 the gas. The print-out system can be provided by adding a gas-generating light-sensitive material to the top layer and then overcoating the top layer with a gas-impermeable film.

The temporary image formed by the construction of  
25 the present invention is provided between the layer containing the photosensitive gas-generating material and the barrier layer. This is significantly different from normal vesicular imaging in which the bubbles of gas are usually trapped within the layer which generates the gas.

30 The barrier layer also does not have to be completely impervious to the generated gas. This is because the quasi-vesicular image formed is only temporarily required and may in fact desirably wash away (e.g., by removal of the barrier layer) in subsequent development or  
35 etching baths. The image formed can also be allowed to disappear by migration and evacuation of the temporarily trapped print-out image forming gas from beneath the

barrier layer. The barrier layer therefore need only be sufficiently impermeable to the generated gas to provide an image for a few minutes. Thus a top coat over the gas-generating layer which had a mass transfer constant or permeability constant as defined in U.S. Patent No. 3,032,414 of not greater than

$$P_{\max} = 1 \times 10^{-9} [\text{cm}^3 \text{ cm}^{-2} \text{ sec}^{-1} (\text{cm Hg/cm}^{-1})]$$

preferably  $1 \times 10^{-10}$  and more preferably  $8 \times 10^{-10}$ . This constant must be satisfied by the binder component of the layer if used as such, or by the layer with a modifier admixture added to a binder.

While the above upper limit of  $P = 8 \times 10^{-10}$  is fairly critical, a lower limit is not equally well defined or critical; however materials with constants below  $P_{\min} = 8.6 \times 10^{-16}$  in most instances will be unsatisfactory.

The above values for  $P$  are referred to temperatures of approximately  $30^\circ\text{C}$ . They also generally refer to nitrogen, the gas which is at the present time most practical for purposes of scatter photography, although other gases such as  $\text{CO}_2$  have been used. These  $P$  values for nitrogen diffusion however are, within the range specified, sufficiently close to those for other gases so that they serve satisfactorily for selecting a proper unmodified vehicle or for compounding with a modifier a vehicle that in itself does not conform to this permeability requirement.

The above permeability limits determine usefulness mainly as to photographic sensitivity and resolution. In general, these improve as the permeability is reduced. Furthermore copies which are thermally stable at ordinary storage temperatures are obtainable within these permeability ranges. To increase permeability with a modifier to permit fixing, an alternate type of modification is possible. A given resin may have permeability

higher than the upper limit of the operating range. This can be brought within the operating range by adding a modifier of low permeability. Thus the modifier is a method of adjusting the over-all permeability to some desired value.

5           The hardness of the vehicle polymer is not very critical with regard to permanence, since it is usually removed.

Vehicle materials according to the invention are further characterized, in purely physical, structural, 10 terms, as primarily highly linear and saturated hydrocarbon chains essentially without crosslinking, such as obtained by polymerization of monomers with substituent groups preferably of small dimensions, made up of only a few elements and few atoms, and in many cases of a moderately 15 electronegative character, imparting the polymer with a certain amount of polarity, or strong interchain cohesion, favoring close molecular fit and crystallinity, with closely adjacent molecule portions forming randomly distributed elementary structures interspersed with 20 randomly distributed areas of lower coherence. These low cohesion areas are believed to constitute, or at least to favor the formation of, nucleating areas where the above described gas units tend to form. Many of the usable materials result from the interpolymerization of two 25 ethylenic monomers resulting in the desirable properties of solubility, and color stability.

The gas-generating material may be any light-sensitive compound or mixture of compounds which generates a gas at standard temperature and pressure when irradiated. 30 Halogen gas liberators, carbon monoxide or carbon dioxide liberators and any other such light sensitive gas generators would be useful. Most preferred is the well-known nitrogen liberator, photosensitive diazonium salts. The term photosensitive diazonium salts refers to all light- 35 sensitive, aromatic diazonium compounds which generate nitrogen gas when struck by electromagnetic radiation, particularly in the visible, ultraviolet and infrared

portion of the spectrum. This includes diazo quinones (encompassing diazo oxides and diazo amides, and diazo sulfides) as well as the more conventional light sensitive aromatic diazonium salts having simple or complex anions. These materials are well-known in the art as represented in U.S. Patent Nos. 4,247,616; 4,193,797; 4,189,320; 4,039,521; and 3,282,939 as well as in Light-Sensitive Systems, Kosar, John Wiley and Sons, Inc., 1965, pp. 202-214 and 276-282.

The various photosensitive imaging systems known to use these gas-generating materials which can make use of the present invention include for example, positive-acting photoresist systems (e.g., U.S. Patents 4,247,616 and 4,193,797), negative acting photoresists, and lithographic compositions (e.g., U.S. Patent 4,104,072 and Belgian Patent No. 881,956), diazonium-coupler dye forming systems (e.g., U.S. Patent Nos. 4,230,789; 4,168,171; 3,754,916; and 3,199,982) and dye bleach systems or leuco dye oxidation systems as known in the art. Each of these systems uses a diazonium salt as an ingredient in a light-sensitive non-vesicular layer.

The invention may be most readily practiced by bonding the layer which is resistant to penetration of nitrogen gas as close as possible to or directly on the surface of the layer containing the gas generating photosensitive compound. Thus, the barrier is contiguous to the gas-generating layer. The best mode of positioning the barrier layer is on the surface of the imaging, gas-generating layer. The presence of intermediate layers, such as primer layers, tends to allow the gas to diffuse horizontally and reduce the quality of the image. In any case, intermediate layers should be less than 0.1 mm in thickness and preferably less than 0.05 mm. The intermediate layer should be permeable to nitrogen, for if it is not, it will act in the manner of a barrier layer and form a temporary image.

The barrier layer may be any natural or synthetic organic polymeric optically transmissive layer. Transparent binders and polymers such as polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, methyl vinyl ether  
5 copolymers, polyvinylidene chloride, acrylic latexes, and the like are most preferred. It is also particularly desirable to use solvent systems in laying down the barrier layer which do not penetrate the image forming layer. Since many imaging systems use organic solvents, a water-soluble or water-dispersible top-coat, for example, those  
10 of polyvinyl alcohol or polyvinylpyrrolidone or various latices are particularly desirable. It is generally preferred that the barrier layer be transparent, but there are circumstances where translucency or transparency to  
15 only a limited range or wavelengths would be desirable. As long as the barrier layer allows some activating energy and preferably as portions of the visible spectrum to pass therethrough, the print-out image can be visible. The barrier layer is generally between 0.05 and 300 micrometers  
20 and preferably between 0.05 and 20 micrometers, more preferably between 0.10 and 5.0 and most preferably between 0.10 and 1.0 microns.

In a preferred practice of the invention, matting agents are added to the barrier layer. This provides a  
25 non-glossy appearance to the imageable element and can provide a control on the friction characteristics of the surface. Furthermore, if the material is to be stacked or rolled, the protuberance of the matting agent will prevent or reduce adherence between layers caused by the exclusion  
30 of air between them. Typical photographic matting agents such as polymethylmethacrylate and its copolymers, silica, and the like are generally useful.

One particularly beneficial side effect of the present invention with positive resist systems is enhanced  
35 developability in the imaged (irradiated) areas. This occurs because the vesicles produced by the generated gas are coincident with the more readily washed away portions

0087309

of the light sensitive layer. The top coat is therefore most easily removed in the exposed areas because of reduced adhesion where the positive-acting radiation sensitive layer is also most readily etched or washed away.

5           The following examples further illustrate practice of the present invention.

Example 1

10           Using the apparatus described in U.S. Patent No. 4,268,541 without a baffle, a  $10^{-4}$ m polyester web was coated by vacuum deposition with 70nm of aluminum. During the same operation in the same vacuum chamber a layer of a commercially available terpolymeric acrylate material (derived from 62% methylmethacrylate, 36% n-butylacrylate and 2% acrylic acid by weight) was applied. This sample  
15           represents an article made according to the teachings of U.S. Patent 4,268,541. A control length of non organic-coated aluminum film was also produced. Ellipsometric measurements of the resultant organic/metal package indicated that the thickness of the acrylate layer was  
20           30.5nm.

25           The resultant aluminum plus organic coated material was examined by way of transmitted light and exhibited very few pinholes or defects. The otherwise soft aluminum layer of this package could not be rubbed off using thumb pressure. The non organic coated aluminum film could be rubbed off using thumb pressure.

30           Both the organic vapor coated sample and the unprotected sample were immersed in a bath of 1.2% sodium hydroxide and 3% of the tetra sodium salt of nitrilo-triacetic acid at 32°C. The unprotected Al layer was uniformly, cleanly oxidized away in 15 seconds. The organic-protected layer was not cleanly removed. In fact, the aluminum lifted off in sections during the immersion time and then the aluminum generally oxidized in solution.

Example 2

Using the apparatus described in the Example 1, a 2000 meter continuous web was vapor coated with a 70nm layer of aluminum and immediately thereafter in the same chamber, a 10 nm layer of terephthalic acid was applied. At the 1400 meter level, the terephthalic coated roll telescoped on itself and telescoped further when removed from the chamber. After removal from the chamber, the vapor-coated aluminum/terephthalic acid roll was judged to be unacceptable for production purposes.

Example 3

Using the technique described in Example 1, three more rolls of 2000 meters were coated and a different organic material applied to the aluminum of each of these rolls. Roll A contained an organic layer (on top of the aluminum layer) consisting of Resinox, a phenol formaldehyde condensate resin made by the Monsanto Corp.

Roll B was identical to Roll A except than an organic layer of Vitel 200, a low molecular weight polyester resin (approximately 10,000 molecular weight) made by and commercially available from Goodyear was applied to the aluminum layer. Roll C consisted of a control roll of vapor-coated aluminum film identical to rolls A and B with no organic protective coating.

None of these three rolls telescoped.

Example 4

Using the apparatus of Example 1, the following materials were applied to vapor-coated aluminum webs in various thicknesses from 15 to 250 nm.

- 1) Dimethyl terephthalate
- 2) Phthalic anhydride
- 3) Mono methyl phthalate

- 4) Dapon 35 - a diallyl phthalate prepolymer made by FMC Corp.
- 5) Bisphenol A
- 6) Epon 828 - an epoxy resin made by the Shell Corp.
- 5 7) Michlers Ketone
- 8) Benzophenone
- 9) Benzyl alcohol
- 10) Salacylamide

These materials were unrolled after coating and inspected with a 10X hand lens by transmitted light. The defects in an area of 177mm<sup>2</sup> were counted and compared to those of a non organic coated aluminum film prepared as a control. The control film exhibited defect levels over 100. The materials tested had defect levels of 30 or less. The control material that had no protective layer could be rubbed off using thumb pressure - the organic protective material could not. None of the above materials felt slippery and none produced any telescoping during or after rolling.

## 20 Example 5

Using the apparatus of Example 1, two coatings were made on top of a 70nm aluminum layer, one using a protective coating of Resinox as the organic layer; another using terephthalic acid as the organic layer. Both these organic layers were applied to produce an organic layer of about 5nm thickness as determined by a Gaertner Ellipsometer.

These two webs were further coated with a resist layer of the type described in our copending application S.N. 350,737, filed in 1982. A control web consisting of only the 70 nm aluminum layer was prepared as well.

After coating and drying these films were exposed to a 10 step Stauffer grey scale using a 2kw Berkey Ascor printing source (light to film distance 1 mtr) for 15 seconds. The exposed films were developed in the

processing solution described in Example 1 of U.S. Patent No. 4,314,022 for 30 sec, at 38°C followed by a warm water wash. On inspection it was evident that the Resinox and control film had grey scale values of step 5, the  
5 terephthalic acid roll however had a grey scale value of 7 indicating a faster, more uncontrolled development.

Example 6

Using the technique of Example 1, a Vitel 200 polyester coating was applied in a thickness of 10 nm to  
10 various metal layers including

- 1) Tin
- 2) Copper
- 3) Aluminum/Mg (Al 94.8%; Mg 5.0%; Mn 0.1%; Cr 0.1%)
- 4) Aluminum plus Iron (ratio  $Al_2Fe_5$ )
- 15 5) Nickel

A control non-organic coated layer was included for each metal while thumb action rubbing was able to remove the unprotected metal. The protected metal layers (organic coated) would not rub off.

20 Example 7

Using the technique described in Example 1, 4 separate, 30 meter,  $10^{-4}$ m polyester base samples were continuously vapor-coated with aluminum (thickness 70nm). One of these was additionally vapor-coated (in the same  
25 pass time and vacuum chamber as the Al layer) with a 30nm layer of a 62/36/2 methylmethacrylate/n-butylacrylate/-acrylic acid terpolymer (henceforth called Sample A). The second web was additionally vapor-coated with a 30nm layer of terephthalic acid (in the same pass time and vacuum  
30 chamber as the aluminum layer - henceforth called Sample B). The 3rd sample called C was made identical to Sample B but the thickness of terephthalic acid was reduced to 10nm.

The 4th sample (D) was not overcoated with an organic protective layer. All of the above webs were wound up in vacuum under a tension equal to 40 lbs.

Sections of all of the samples were unrolled and viewed on a graphic light source and inspected using a 10X hand magnifying glass. Scratches, cinch marks, and other defects were counted on different areas of each web.

Select areas of 177mm<sup>2</sup> were viewed and the defects counted. Table 1 list the defect levels of each web.

TABLE 1

<u>SAMPLE</u>	<u>DEFECT LEVEL</u>
A	18
B	17
C	17
D	100

All of the above webs were coated with the photoresist of Example 3 of U.S.S.N. 350,737, filed in 1982 at a coating weight of 281 mg/ft<sup>2</sup>. After coating, each of these samples was exposed to a 10 step Stauffer grey scale using a Berkey Ascor 2kw commercial light source (lamp to film distance 1 meter) using a metal halide lamp for a period of 15 seconds. After exposure, these films were developed in a Graphic Arts rapid access processor. Processing conditions include a 60 second development time using the developer solution of Example 1 of U.S. Patent No. 4,314,022 at 39°C followed by a 30 second wash cycle. The 10 step grey scale reproductions on each of these films was examined. Table 2 details these results.

TABLE 2

	<u>SAMPLE</u>	<u>STEPS SEEN</u>	<u>COMMENTS</u>
	A	2	Large areas removed non imagewise
5	B	7	3-5% dots undercut
	C	4	Good sharp 3% dots
	D	4	Equal dots to Sample C

These data clearly indicate that the higher coating levels of organic protective material taught in U.S. Patent 4,268,541 interfere with development, producing inferior reproductions, although they adequately protect the Al web from defects.

Example 8

Using the technique described in Example 1, eight separate, 30m polyester base samples were continuously vapor-coated with different metals of nominally the same thickness as in Example 1. One sample of each of the following metal layers was overcoated with a protective layer.

	<u>SAMPLE</u>	<u>METAL</u>
	1	Tin
	2	Copper
	3	Aluminum
	4	Aluminum/Magnesium
25		(Al 94.8%; Mg 5.0%; Mn 0.1%; Cr 0.1%)
	5	Al <sub>2</sub> Fe <sub>5</sub>

The protected layer films had a 8nm layer of terephthalic acid vapor-coated on top of the metal layer. At the same time, the metal layer was vapor-coated in the same pass and vacuum chamber. A 10X inspection of a 177mm<sup>2</sup> area of each

of the webs placed over a lighted table indicated the following defect levels.

<u>DEFECT COUNTS/177mm<sup>2</sup> AREA</u>		
<u>METAL</u>	<u>PROTECTED LAYER</u>	<u>UNPROTECTED LAYER</u>
5 Tin	19	170
Copper	22	163
Aluminum	18	135
Aluminum/Magnesium	20	142
Aluminum/Iron	19	150

10 Example 9

Using the technique of Example 1, several different materials were in-line, in situ vapor-coated on top of a 70nm layer of aluminum at the time the aluminum layer was applied. These were applied in 2 levels, a level of 8nm and a level of 30nm and wound up in a roll from under a take-up roll tension of 40 pounds.

- 1) Terephthalic acid
- 2) Salicylic acid
- 3) Terpolymer of 62% by weight methyl methacrylate, 36% n-butylacrylate, and 2% acrylic acid
- 4) Behenic acid

After application, each of these samples were perused with a 10X hand lens and defect counts conducted in areas of 177mm<sup>2</sup>. The following table details the observation of these studies as well as additional notes. The data was compared to a web coated with aluminum of the same thickness and at the same thickness and at the same time as the other samples.

DEFECT COUNTS ON TREATED VAPOR-COATED METAL LAYERS

	<u>Material</u>	<u>Untreated</u>	<u>Level 8nm</u>	<u>Level 30nm</u>	<u>Notes</u>
	Unprotected				
	Aluminum	1000	-----	-----	-----
5	Terephthalic acid	-----	20	23	30nm level; powdery, not optically clear; both slippery.
10					
	Salicylic acid	-----	23	22	30nm level; slippery; roll telescoped.
15					
	Acrylate Terpolymer	-----	18	21	removed from base in chunks by developer (30nm)
20					
	Behenic acid		20	23	30nm level tacky.
25					
30	The above data show that the thickness range of 8 to less than 30nm provides excellent protection against abrasion defects but that the thicker layer tends to create other difficulties such as reduced optical clarity, excessive slipperiness and tackiness.				

## CLAIMS:

1. A process for improving the abrasion resistance of vapor deposited metal layers which comprises vapor depositing a metal layer on at least one surface of a substrate and, before subjecting the metal layer to physical treatment or contact which would abrade the metal layer, vapor depositing onto said metal layer 1) a 1 to 600 nm layer of organic material having a vapor pressure at 20°C equal to or less than that of 1-n-octanol said material having a) a carbonyl group not part of a carboxyl group, b) a phenoxy group, c) an ester group, or d) an alcohol group, or 2) a layer of organic material having a thickness of at least 1 nm and less than 30 nm and a) a carboxyl group, b) a saccharide, c) Rhodamine B, or d) phthalocyanine.

2. The process of claim 1 wherein at least 75% of the thickness of said metal layer consists essentially of a material selected from the group consisting of metals, metal compounds, metal salts and combinations thereof.

3. The process of claim 1 wherein said metal layer consists essentially of a material selected from the group consisting of metals, metal compounds, metal salts, and combinations thereof.

4. The process of claims 1, 2, or 3 wherein said organic material is selected from the group consisting of amides, anilides, bisphenol A, phenol formaldehyde resins, low molecular weight polyesters, and alcohols having a vapor pressure at 20°C no higher than 1-n-octanol.

5. The process of claims 2 or 3 wherein said organic material is selected from the group consisting of alkyl esters of carboxylic acids, polyester oligomers, and polyester polymers.

0087309

6. The process of claims 2 or 3 wherein said organic material is selected from the group consisting of aliphatic carboxylic acids, aromatic carboxylic acids, and acrylic or methacrylic polymers or copolymers.

5           7. An article comprising a substrate having on at least one surface thereof a vapor deposited metal layer and adhered to said metal layer 1) a layer of 1 to 600 nm comprising an organic material having a vapor pressure at 20°C less than or equal to that of 1-n-octanol and having  
10   a) a carbonyl group which is not part of a carboxyl group, b) a phenoxy group, c) an ester group, or d) an alcohol group, or 2) a layer of organic material having a thickness of at least 1 nm and less than 30 nm and a) a carboxyl  
15   group, b) a saccharide, c) Rhodamine B, or d) phthalocyanine.

8. The article of claim 8 wherein said metal layer consists essentially of a material selected from the group consisting of metals, metal compounds, metal salts and combinations thereof.

20           9. The article of claims 7 or 8 wherein said organic material is selected from the group consisting of amides, anilides, bisphenol A, phenol formalde resins, polyester resins having a molecular weight between 5,000 and 50,000, and alcohols having a vapor pressure at 20°C no  
25   higher than that of 1-n-octanol.

10. The article of any one of Claims 7 to 9 having coated over said organic material a photoresist layer.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0087309  
Application number

EP 83300897.2

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
D, X	<p>US - A - 4 268 541 (T. IKEDA et al.)</p> <p>* Totality; especially column 1, lines 14-40 *</p> <p>----</p>	1-10	<p>C 23 C 13/04</p> <p>C 23 C 13/02</p> <p>B 05 D 1/36</p>
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			<p>C 23 C</p> <p>B 05 D</p>
The present search report has been drawn up for all claims			
Place of search:		Date of completion of the search	Examiner
VIENNA		19-04-1983	SLAMA
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone		T : theory or principle underlying the invention	
Y : particularly relevant if combined with another document of the same category		E : earlier patent document, but published on, or after the filing date	
A : technological background		D : document cited in the application	
O : non-written disclosure		L : document cited for other reasons	
P : intermediate document		& : member of the same patent family corresponding document	